

# AMENDED SPECIFICATION

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## PATENT SPECIFICATION

1093.376

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### NO DRAWINGS

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Int. Cl.:—C 07 d 55/12

### COMPLETE SPECIFICATION

#### Substituted 1,3,5-Triazine Compounds and Pesticidal Preparations containing them

We, CIBA LIMITED, a body corporate organised according to the laws of Switzerland, of Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention provides a pesticidal preparation, especially a herbicidal or microbicidal preparation, which comprises as active substance a compound of the general formula



(1)

wherein R<sub>1</sub> represents a halogen atom, an azide radical, an aliphatic hydrocarbon radical containing up to 4 carbon atoms, the group —ZX

(wherein Z stands for oxygen or sulfur and X for an aliphatic hydrocarbon radical containing up to 4 carbon atoms, R<sub>2</sub> represents an aliphatic hydrocarbon radical containing up to 4 carbon atoms, the group —ZX (wherein Z stands for oxygen or sulphur and X for an aliphatic hydrocarbon radical containing up to 4 carbon atoms) or represents the group



(wherein A<sub>1</sub> stands for an aliphatic hydrocarbon radical containing up to 4 carbon atoms, an alkoxyalkyl, hydroxyalkyl, cyanoalkyl or alkylthioalkyl group containing not more than 4 carbon atoms, A<sub>2</sub> stands for a hydrogen atom or has the same meaning as A<sub>1</sub>, together with a suitable carrier. There may also be present, in the preparations, one or more of the following additives: a solvent, a diluent, a dispersant, an adhesive and/or another pesticide, especially a herbicide or a fungicide.

The present invention provides especially

those preparations of the kind defined above which contain as active substance a compound of the general formula



(II)

- 5 wherein  $X_1$  represents a lower alkyl or alkenyl radical containing up to 4 carbon atoms, and R represents an amino group substituted by a lower alkyl or alkenyl radical containing up to 4 carbon atoms.

- 10 The preparations preferably contain, as active ingredient, those of the compounds referred to above wherein  $X_1$  is a methyl group. Also, especially interesting compounds that may be present as active substances in the preparations are those of the general formula:—



(V)

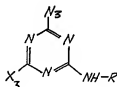
- 20 wherein  $X_2$  represents a saturated or unsaturated aliphatic hydrocarbon radical containing up to 4 carbon atoms, an alkoxyalkyl radical containing up to 4 carbon atoms or a chloroalkyl radical containing up to 4 carbon atoms, and R represents the azide radical or the group



25

- wherein  $A_1$  stands for a saturated or unsaturated aliphatic hydrocarbon radical containing up to 4 carbon atoms, or an alkoxyalkyl radical, and  $A_2$  for a hydrogen atom or an alkyl radical containing up to 4 carbon atoms.

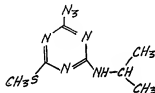
- 30 Preparations having a particularly good herbicidal effect are those containing the compounds of the following general formula



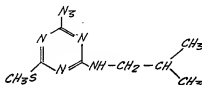
(VI)

wherein R represents an alkyl radical containing up to 4 carbon atoms, and  $X_3$  stands for a chlorine atom or the group  $CH_2-S-$  or the azide radical. Among these compounds, the following are distinguished by their special potency:

40



and



The new compounds of the general formula (I) can be prepared by methods known *per se*, for example by reacting a compound of the general formula

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or



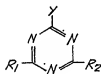
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wherein  $R_1$  and  $R_2$  have the same meanings as in the above general formula (I) and  $X_4$  represents a halogen atom or a quaternary ammonium group—with an alkali metal azide, for example  $NaN_3$ , preferably in a homogeneous or heterogeneous solvent phase, for example acetone+water, dioxane+water or dimethylformamide, with cooling or heating, preferably at a temperature ranging from  $-30^\circ$  to  $100^\circ C$ .

55

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Another process for the manufacture of the active substances of the formula (I) comprises reacting a compound of the formula



or



wherein R<sub>1</sub> and R<sub>2</sub> have the above meanings and Y stands for a hydrazino group, with nitrous acid or a nitrous acid donor. Particularly suitable nitrous acid donors are the salts of this acid, and this reaction is carried out in an aqueous, acid solution.

Furthermore, there may be used for this purpose an alkylnitrite for example ethylnitrite, butylnitrite or amylnitrite in an alcoholic solution.

The present invention further includes the use of the compounds of the above formula (I) for combating pests, especially undesired plant growth, and harmful micro-organisms for example bacteria and fungi, insects, for example *Musca domestica*, acarides for example spinner mites, nematodes and molluscs, for example land and water snails.

It is a special advantage of the active substances of the above formula (I) and of the preparations containing these active substances that they may be used not only as total herbicides but, when used in a suitable concentration, also as selective herbicides. Thus, it is possible, for example, to combat successfully undesired plant growth in cultures of useful plants without appreciably damaging the latter.

The preparations of this invention may be applied in a wide variety of forms. For manufacturing solutions of compounds of the general formula (I) for direct spraying there may be used, for example, petroleum fractions of a medium to high boiling range, preferably above 100°C for example Diesel oil or kerosene, coal tar oils and oils of vegetable or animal origin, also hydrocarbons for example alkylated naphthalenes, tetrahydronaphthalene, if desired in combination with xylene mixtures, cyclohexanols, ketones, also chlorinated hydrocarbons for example trichloroethane, tetrachloroethane, trichloroethylene, trichloro-

benzenes or tetrachlorobenzenes.

Aqueous forms of applications are prepared, for example, by adding water to emulsion concentrates, pastes or wettable spray powders. Suitable emulsifiers or dispersants are, for example, nonionic products, such as condensation products of ethylene oxide with aliphatic alcohols, amines or carboxylic acid containing a long-chain hydrocarbon radical with about 10 to 20 carbon atoms, for example the condensation product of octadecyl alcohol with 25 to 30 mols of ethylene oxide, or of soybean fatty acid with 30 mols of ethylene oxide, or of commercial oleylamine with 15 mols of ethylene oxide, or of dodecylmercaptan with 12 mols of ethylene oxide. As examples of suitable anionic emulsifiers there may be mentioned the sodium salt of the dodecyl alcohol sulfuric acid ester, the sodium salt of the dodecylbenzenesulfonic acid, the potassium or triethanolamine salt of oleic acid or of abietic acid or of mixtures of these two acids, or the sodium salt of a petroleum sulfonic acid. Suitable cationic dispersants are quaternary ammonium compounds for example cetyl pyridinium bromide and dihydroxyethyl benzyl dodecyl ammonium chloride.

Dusting and casting preparations may contain as solid vehicles talcum, kaolin, bentonite, calcium carbonate or calcium phosphate, also coal, cork meal, wood meal and other materials of vegetable origin. It is also very advantageous to manufacture the preparations as granulates. The diverse forms of applications may contain the usual substances capable of improving the distribution, the adhesion, the stability towards rain or the penetration; as such substances there may be mentioned fatty acids, resins, glue, casein and alginates.

The preparations of the invention may be used by themselves or in combination with conventional pesticides, especially insecticides, acaricides, nematocides, bactericides or further fungicides and/or herbicides.

Weeds that can be controlled with the preparations of this invention include also undesired culture plants, for example such as have been planted previously on the soil to be treated. The preparations may be used both by the pre-emergence and the post-emergence method.

The present invention therefore also includes a method of selectively combating weeds in a crop area by treating the crop area with a preparation as hereinbefore defined.

The present invention further includes the new compounds of the general formula (I) as such.

The following Examples illustrate the invention. Unless otherwise indicated, parts and percentages in the above description and in the following Examples are by weight.

## EXAMPLE 1

- (1) Azido - 4 - chloro - 6 - ethylamino - 1,3,5-triazine

A solution of 12 parts of sodium azide in 100 parts of water was mixed dropwise with a solution of 19.6 parts of 2,4 - dichloro - 6 - ethylamino - 1,3,5 - triazine in 50 parts by volume of acetone while stirring vigorously, with the temperature of the suspension rising to 31°C. The mixture was stirred for 1 hour at this temperature and then filtered. The product was crystallized from alcohol; it melted at 97° to 98°C. The following compounds were manufactured in an analogous manner:

- (2) 2 - Azido - 4 - n - butylamino - 6 - chloro - 1,3,5 - triazine, melting at 76° to 77°C., from alcohol,

- (3) 2 - Azido - 4 - chloro - 6 - isobutylamino - 1,3,5 - triazine, melting at 110° to 111°C, from cyclohexane, and

- (4) 2 - Azido - 4 - secondary butylamino - 6 - chloro - 1,3,5 - triazine, melting at 48° to 52°C, from hexane. The 2,secondary butylamino-4,6-dichloro-1,3,5-triazine required as

intermediate for the manufacture of compound No. 4 was prepared as described by J. T. Thurston et al., in J. Am. Chem. Soc. 73, page 2981 [1951]. The product was extracted from the reaction mixture with chloroform and then distilled; it boils at 108° to 110° under 0.07 mm Hg pressure.

- (5) 2 - Azido - 4 - tertiary butylamino - 6 - chloro - 1,3,5 - triazine, melting at 73—76°C (hexane)

- (6) 2 - Azido - 4 - fluoro - 6 - isobutylamino-1,3,5-triazine

While cooling a mixture of 135 parts of cyanuric fluoride and 1000 parts by volume of acetone with ice, 147 parts of isobutylamine were dropped in. On completion of the reaction the mixture was filtered, and the filtrate evaporated; the residue taken up in 500 parts by volume of toluene and washed with ice water. The solution was dried with anhydrous sodium sulfate and evaporated. The resulting 2,4 - difluoro - 6 - isobutylamino - 1,3,5 - triazine was distilled under a high vacuum; it boiled at 90° to 92°C under 0.2 mm Hg pressure and melted at 41° to 43°C.

26 parts of 2,4 - difluoro - 6 - isobutylamino-1,3,5-triazine were dissolved in 50 parts by volume of acetone and 10 parts of sodium azide and 10 parts of water were stirred in, while maintaining the temperature below 52°C by cooling. The mixture was then stirred for 24 hours at room temperature, mixed with 200 parts of water, the precipitate formed was filtered off, dried and repeatedly recrystallized from hexane and cyclohexane. It melted at 100° to 103°C.

- (7) 2 - Azido - 4 - bromo - 6 - isobutylamino-1,3,5-triazine

57.5 Parts of isobutylamine were added dropwise at 0°C to a suspension of 125 parts

of cyanuric bromide in 400 parts by volume of acetone, and the mixture was then stirred for 4 hours at room temperature, filtered and the filtrate was evaporated. The residue was dissolved in 750 parts by volume of toluene and washed with ice water. The solution was dried over anhydrous sodium sulfate and evaporated. The resulting 2,4 - dibromo - 6 - isobutylamino - 1,3,5 - triazine was crystallized from cyclohexane; it melted at 92° to 94°C.

46.5 Parts of 2,4 - dibromo - 6 - isobutylamino-1,3,5-triazine were dissolved in 60 parts by volume of acetone and 10 parts of sodium azide and 20 parts of water were stirred in. The mixture heated up to 41°C and was then stirred for 24 hours at room temperature. The product was taken up in 200 parts by volume of toluene and washed with 2x100 parts of water. The solution was evaporated. The resulting 2 - azido - 4 - bromo - 6 - isobutylamino-1,3,5-triazine was crystallized from petroleum ether; it melted at 83° to 87°C.

- (8) 2 - Azido - 4 - isopropylamino - 6 - methyl-1,3,5-triazine

A solution of 41 parts of 2,4-dichloro-6-methyl-1,3,5-triazine in 400 parts by volume of acetone was mixed dropwise with 30 parts of isopropylamine, while cooling to maintain the temperature at about 25°C. The mixture was then further stirred for 5 hours at room temperature, filtered and evaporated. The residue was dissolved in 300 parts by volume of hexane. The solution was washed with ice water, dried over anhydrous sodium sulfate, filtered and evaporated. The resulting 2-chloro - 4 - isopropylamino - 6 - methyl - 1,3,5-triazine was distilled; it boiled at 143° to 146° under 16 mm Hg pressure and melted at 45° to 47°C.

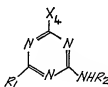
A solution of 34.5 parts of 2-chloro-4-isopropylamino - 6 - methyl - 1,3,5 - triazine in 700 parts by volume of dry toluene was mixed at about 5°C with 100 parts by volume of 4-molar toluolic trimethylamine solution. The mixture was kept for a few hours at 5°C and then for 2 days at room temperature. The precipitated quaternary ammonium salt was filtered off and dried in a high vacuum at room temperature.

A solution of 24.6 parts of 6-(2-isopropylamino - 4 - methyl - 1,3,5 - triazinyl) - trimethyl ammonium chloride in 50 parts of water was mixed with 12 parts of sodium azide, and the mixture stirred for 3 hours at 50°C and allowed to cool. The precipitate was filtered off, washed with water, dried and crystallized from hexane. It melted at 71°—72°C.

- (9) 2 - Azido - 4 - ethylamino - 6 - methylmercapto-1,3,5-triazine

A solution of 39.9 parts of 2,4-dichloro-6-methylmercapto-1,3,5-triazine in 120 parts by volume of siloxane was vigorously stirred drop-

- wise at about 10°C into a mixture of 13 parts of ethylamine of 70% strength and 200 parts of water. 100 Parts by volume of 2N-sodium hydroxide solution were then added portion-
- 5 wise and the temperature allowed to rise to 20°C. When the sodium hydroxide solution was consumed, 20 parts of solid sodium azide were added and the emulsion stirred for 6
- 10 hours at about 75°C. The mixture was then cooled. The precipitated product was filtered off and washed with 2X100 parts of water, then crystallized from methanol, whereupon it melted at 114° to 116°C.
- 15 In an analogous manner the following compounds were manufactured from 2,4-dichloro-6-methylmercapto-1,3,5-triazine and the corresponding amines:
- (10) 2-Azido-4-methylamino-6-methylmercapto-1,3,5-triazine, melting at
- 20 164° to 165°C, from alcohol
- (11) 2-Azido-4-methylmercapto-6-n-propylamino-1,3,5-triazine, melting at 104° to 105°C from methanol
- 25 (12) 2-Azido-4-isopropylamino-6-methylmercapto-1,3,5-triazine, melting at 92° to 94°C, from cyclohexane
- (13) 2-Azido-4-n-butylamino-6-methylmercapto-1,3,5-triazine, melting at
- 30 93° to 95°C, from methanol
- (14) 2-Azido-4-isobutylamino-6-methylmercapto-1,3,5-triazine
- A solution of 196 parts of 2,4-dichloro-6-methylmercapto-1,3,5-triazine in 1000 parts by volume of benzene was mixed drop-wise with 146 parts of isobutylamine, while cooling
- 35 externally to maintain a temperature below 20°C. The mixture was then stirred at room temperature until no more free amine could be identified, and filtered. The filtrate was washed with ice water, dried over anhydrous sodium sulfate and evaporated, the residue being
- 40 crystallized from hexane. The resulting 2-chloro-4-isobutylamino-6-methylmercapto-1,3,5-triazine melted at 109° to 111°C.
- A mixture of 30 parts of 2-chloro-4-isobutylamino-6-methylmercapto-1,3,5-triazine, 50 parts of sodium azide, 150 parts by volume of dioxane and 150 parts by volume of water was stirred for 24 hours at 80°C. The
- 45 product was extracted with 300 parts by volume of toluene. The extract was washed with 2X100 parts of water, dried over anhydrous sodium sulfate and evaporated. The resulting 2-azido-4-isobutylamino-6-methylmercapto-1,3,5-triazine melted at 102°
- 50 to 103°C, and after crystallization from cyclohexane at 102° to 104°C.
- In an analogous manner, the compounds listed in the following Table were manufactured, using as starting material 2-alkylmer-
- 60 capto-4,6-dichloro-1,3,5-triazines:



	R <sub>1</sub> =	R <sub>2</sub> =	X <sub>4</sub> =Cl; m.p. °C	X <sub>4</sub> =N <sub>3</sub> ; m.p. °C
(15)	methylmercapto	sec. butyl	39—42° (b.p. 122° 0.5mm Hg)	69—71° petroleum ether
(16)	methylmercapto	β-methoxy- ethyl	85—87° hexane	90°, methanol
(17)	methylmercapto	γ-methoxy- propyl	68—69° cyclo- hexane	59—60° cyclohexane
(18)	methylmercapto	β-methyl- mercapto- ethyl	92—94° cyclo- hexane	94—95° alcohol
(19)	isopropylmer- capto	γ-methoxy- propyl	72—74° hexane	74—75° methanol
(20)	n-butylmercapto	"	63—65° cyclo- hexane	34—36° hexane
(21)	sec. butylmer- capto	"	58—60° petroleum ether	52—53° petroleum ether

- (22) In the same manner, using as starting material 2,4 - dichloro - 6 - methylmercapto - 1,3,5-triazine, there was obtained via the immediately formed 2 - chloro - 4 - diethylamino - 6 - methylmercapto - 1,3,5 - triazine (from petroleum ether, m.p. 53—55°C) the 2-azido - 4 - diethylamino - 6 - methylmercapto-1,3,5-triazine; this compound was liquid and displayed in the infrared spectrum a strong band at 4.66μ.
- (23) (a) 2 - secondary butylmercapto - 4 - chloro - 6 - isopropylamino - 1,3,5-triazine
- 15 107 Parts of 2-secondary butylmercapto-4,6-dichloro-1,3,5-triazine were mixed with 750 parts by volume of anhydrous toluene, and 53.2 parts of isopropylamine were gradually stirred in, while cooling with ice to maintain a temperature of about 150°C. The batch was then allowed to react for another 30 minutes at room temperature. The precipitate was filtered off, the filtrate evaporated, and the residue distilled in a high vacuum.
- 25 2 - secondary Butylmercapto - 4 - chloro-6 - isopropylamino - 1,3,5 - triazine was obtained as a highly viscous oil which distilled at 139°C under a pressure of 0.05mm Hg.
- (b) 6 - (2 - secondary Butylmercapto - 4 - isopropylamino - triazinyl) - trimethyl ammonium chloride
- 30 A solution of 78 parts of 2-secondary butylmercapto - 4 - chloro - 6 - isopropylamino - 1,3,5-triazine in anhydrous toluene was stirred dropwise at -5° to 0°C into a solution of 55 parts of trimethylamine in 500 parts by volume of anhydrous toluene, whereupon the mixture was further stirred for 14 hours at about 20°C. The resulting quaternary salt was
- 35

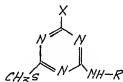
filtered off, washed with toluene and dried in a high vacuum at room temperature.

- (c) 2 - Azido - 4 - secondary butylmercapto - 6 - isopropylamino - 1,3,5-triazine

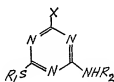
20 Parts of 6 - (2 - secondary butylmercapto - 4 - isopropylamino - triazinyl) - trimethyl ammonium chloride were dissolved at room temperature in 50 parts of water, 17 parts of solid sodium azide were stirred in and the whole was heated for a short time at about 60°C. 100 Parts by volume of benzene and 100 parts of water were then added, the aqueous phase was separated and the benzene

solution dried over anhydrous sodium sulfate, filtered and evaporated. The residue was freed in a high vacuum at room temperature from the last remnants of solvent, to yield pure 2 - azido - 4 - secondary butylmercapto - 6 - isopropylamino-1,3,5-triazine as a viscous oil.

In an analogous manner, using as starting materials 2 - alkylmercapto - 4,6 - dichloro - 1,3,5-triazines, the following compounds were manufactured (the compounds obtained in crystalline form on reaction with sodium azide were filtered off, washed with water, dried and recrystallized).



R =		X = Cl; m.p. °C	X = N <sub>3</sub> ; m.p. °C
(24)	tert. butyl	b.p. 97—98° 0.02mm Hg	59—63° petroleum ether
(25)	β-hydroxy-ethyl	125—126° nitrobenzene	105—109°, methanol
(26)	β,β-dimethoxyethyl	90—91° cyclohexane	88°, methanol
(27)	β-cyanoethyl	133—134°	146—148°, aqueous methanol
(28)	γ-methoxypropyl	68—69° cyclohexane	identical with (17)



	R <sub>1</sub> =	R <sub>2</sub> =	X = Cl; m.p. °C	X = N <sub>3</sub> ; m.p. °C
(29)	ethyl	isopropyl	(b.p. 128°, 0.06mm Hg)	liquid
(30)	isopropyl	isobutyl	97—99° hexane	106—107° methanol
(31)	"	secondary butyl	(b.p. 124°, 0.3mm Hg)	liquid
(32)	n-butyl	isopropyl	(b.p. 123°, 0.1mm Hg)	27—33°
(33)	"	isobutyl	58—59° hexane	60—61° methanol
(34)	"	sec. butyl	(b.p. 158—160° 0.6mm Hg)	liquid
(35)	isobutyl	isopropyl	(b.p. 130° 0.15mm Hg)	"
(36)	"	isobutyl	(b.p. 143—145° 0.2mm Hg); m.p. 45—47°	65—66° methanol
(37)	"	sec. butyl	(b.p. 135° 0.2mm Hg)	liquid
(38)	"	γ-methoxypropyl	46—47° (b.p. 168—169° 0.1mm Hg)	47—48° aqueous methanol
(39)	sec. butyl	isopropyl	127—128° 0.04mm Hg	liquid

(40) (a) 2 - Ethylamino - 4 - hydrazino - 6 - methylmercapto-1,3,5-triazine

10.5 parts of hydrazine hydrate and then 8 parts of sodium hydroxide, dissolved in 20 parts of water, were added dropwise at 30° to 50°C to a solution of 41 parts of 2-ethylamino - 4 - chloro - 6 - methylmercapto - 1,3,5-triazine in 200 parts by volume of dioxane. The mixture was heated for several hours at 55°C and then poured into 600 parts of ice water. The crystalline product was

filtered off, washed with ice water and twice recrystallized from alcohol; it melted at 150 to 151°C.

(40) (b) 2 - Azido - 4 - ethylamino - 6 - methylmercapto-1,3,5-triazine

A solution of 10 parts of 2-ethylamino-4-hydrazino - 6 - methylmercapto - 1,3,5 - triazine in 150 parts by volume of N-hydrochloric acid was mixed at 0° to 5°C dropwise with a solution of 3.5 parts of sodium nitrite in 10 parts of water. The product precipitated



immediately. The resulting 2 - Azido - 4 - ethylamino - 6 - methylmercapto - 1,3,5 - triazine was filtered off, washed with water and crystallized from methanol; it melted at 116° to 117°C and was identical with product (9).

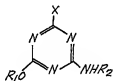
(41) 2 - Azido - 4 - isopropylamino - 6 - methoxy-1,3,5-triazine

A stirred solution of 270 parts of 2,4-dichloro - 6 - methoxy - 1,3,5 - triazine in 1500 parts by volume of toluene was mixed dropwise with 89 parts of isopropylamine and then with 360 parts of sodium hydroxide solution (prepared from 60 parts of sodium hydroxide and 300 parts of water). By cooling with ice the temperature was maintained below 20°C. The mixture was then stirred at about 20°C until a neutral reaction materialized. The organic phase was separated, dried over anhydrous sodium sulfate, filtered and evaporated. The residue was crystallized from hexane and melted at 65° to 66°C; it was 2-chloro - 4 - isopropylamino - 6 - methoxy - 1,3,5-triazine.

A solution of 101 parts of 2-chloro-4-isopropylamino - 6 - methoxy - 1,3,5 - triazine in 1500 parts by volume of anhydrous toluene was mixed at +5°C dropwise with 175 parts of a 4-molar toluene solution of trimethylamine. The mixture was then kept for about 14 hours at room temperature. The precipitated quaternary salt was filtered off, washed with anhydrous toluene and dried in a high vacuum at room temperature.

30 Parts of 6 - (2 - isopropylamino - 4 - methoxy-1,3,5-triazinyl)trimethyl ammonium chloride were dissolved in 200 parts of water, and 20 parts of sodium azide were stirred into the solution. The product settled out immediately. The mixture was heated to 55°C and then left to cool. The resulting 2-azido-4 - isopropylamino - 6 - methoxy - 1,3,5 - triazine was filtered off, washed with water and recrystallized from aqueous methanol; it melted at 125° to 128°C.

The following compounds were manufactured in a similar manner.



	R <sub>1</sub> =	R <sub>2</sub> =	X = Cl; m.p. °C	X = N <sub>3</sub> ; m.p. °C
(42)	ethyl	ethyl	90—91°, hexane	98—99°, cyclohexane
(43)	methyl	n-propyl	64—65°, hexane	73—74°, aqueous methanol
(44)	"	allyl	73—74°, "	102—103°, methanol
(45)	"	n-butyl	53—55° (b.p. 114—116°, 0.1mm Hg)	63—64°, aqueous methanol
(46)	methyl	isobutyl	98—99° hexane	67—69°, aqueous methanol
(47)	"	sec. butyl	(b.p. 109—112°, 0.3mm Hg)	65—66°, aqueous methanol
(48)	"	γ-methoxy-propyl	63—64°, hexane	55—56°, hexane

	R <sub>1</sub> ==	R <sub>2</sub> ==	X = Cl; m.p. °C	X = N <sub>3</sub> ; m.p. °C
(49)	n-propyl	methyl	103—104° cyclohexane	92—94°, methanol
(50)	"	ethyl	64—65° (b.p. 116—120° 0.2mm Hg)	76—77°, "
(51)	"	n-propyl	51—55° (b.p. 132—135° 0.25mm Hg)	61—63°, "
(52)	"	isopropyl	(b.p. 124—128° 0.45mm Hg)	96—97°, "
(53)	"	isobutyl	(b.p. 146—150° 0.5mm Hg)	77—78°, "
(54)	"	sec. butyl	(b.p. 130—133° 0.45mm Hg)	40—41°, "
(55)	"	tert. butyl	(b.p. 118—123° 0.45mm Hg)	liquids, highly viscous
(56)	isopropyl	ethyl	80—81°, hexane	83—85°, methanol
(57)	"	n-propyl	71—72°, hexane	73—75°, "
(58)	"	isopropyl	85—86°, hexane	57—58°, "
(59)	"	n-butyl	73—75°, hexane	64—65°, "
(60)	"	isobutyl	93—95°, hexane	99—100°, "
(61)	"	sec. butyl	66—68°, hexane	91—92°, "
(62)	allyl	ethyl	63—64°, hexane	70—71°, "
(63)	"	n-propyl	49—51° (b.p. 142° 0.7mm Hg)	58—59°, "
(64)	allyl	isopropyl	(b.p. 107—110° 0.2mm Hg)	62—63°, methanol
(65)	"	allyl	42—43° (b.p. 121—128° 0.2mm Hg)	62—63°, "
(66)	"	isobutyl	(b.p. 128—132° 0.1mm Hg)	64—65°, "
(67)	"	sec. butyl	(b.p. 118—120° 0.2mm Hg)	47—48°, "

	R <sub>1</sub> =	R <sub>2</sub> =	X = Cl; m.p. °C	X = N <sub>3</sub> ; m.p. °C
(68)	n-butyl	ethyl	65—68° (b.p. 122—124°, 0.2mm Hg)	69—70°, "
(69)	"	n-propyl	39—41° (b.p. 132—135°, 0.07mm Hg)	54—55°, "
(70)	"	allyl	66—67° (b.p. 132—135°, 0.28mm Hg)	64—65°, "
(71)	"	isobutyl	45—46° (b.p. 148—152°, 0.5mm Hg)	76—77°, "
(72)	"	sec. butyl	50—52° (b.p. 140° 0.3mm Hg)	61—62°, "
(73)	"	tert. butyl	(b.p. 134—136°, 0.35mm Hg)	liquid
(74)	isobutyl	isobutyl	64—65° (b.p. 132—135°, 0.5mm Hg)	70—72°, methanol
(75)	"	sec. butyl	(b.p. 117—119°, 0.1mm Hg)	59—60°, "
(76)	β-methoxy-ethyl	isopropyl	(b.p. 121°, 0.04mm Hg)	78—80°, "

(77) 2 - Azido - 4 - dimethylamino - 6 - isopropoxy-1,3,5-triazine melting at 80° to 82°C (methanol) from 2 - chloro - 4 - dimethylamino - 6 - isopropoxy - 1,3,5 - triazine melting at 105° to 107°C (hexane).

(78) 2,4 - diazido - 6 - ethylamino - 1,3,5 - triazine

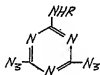
- 10 A solution of 18.4 parts of cyanuric chloride in 70 parts by volume of acetone was added dropwise, while being well stirred, to a solution of 20 parts of sodium azide in 125 parts of water at 0° to 5°C, whereupon the mixture was stirred for a short time. A specimen of the crystalline product was filtered off and crystallized from alcohol; it melted at 94° to 95°C.

The resulting dispersion of 2 - chloro - 4,6-diazido-1,3,5-triazine was dissolved in 200 parts by volume of toluene; this solution was mixed with 6.8 parts of aqueous ethylamine of 70% strength and stirred at 40° to 50°C. During 30 minutes, 50 parts of 2N-sodium hydroxide solution were stirred in portionwise at 40° to 50°C, and the batch was allowed to cool, while being stirred. The organic phase was separated, dried over anhydrous sodium sulfate, filtered and evaporated. The residue was crystallized from methanol or cyclohexane; it melted at 122° to 124°C.

Instead of sodium hydroxide solution, there could have been used an equivalent quantity of ethylamine as hydrochloric acid acceptor;

in this case the batch would have been allowed to react at 40°C, until only a small proportion of free amine remained.

The 2 - alkylamino - 4,6 - diazido - 1,3,5-triazines listed in the following Table were manufactured in a similar manner:



R =		Melting at °C
(79)	methyl	167—168° (methanol)
(80)	n-propyl	134° ( " )
(81)	isopropyl	123—124° ( " )
(82)	allyl	114—115° ( " )
(83)	n-butyl	121—122° ( " )
(84)	isobutyl	115—116° ( " )
(85)	tert.-butyl	69—70° (petroleum ether)
(86)	β-methoxyethyl	118° ( " )
(87)	γ-methoxypropyl	78—79° ( " )

Further manufactured were the following compounds:

- 10 (88) 2 - Diethylamino - 4,6 - diazido - 1,3,5-triazine, melting at 44° to 47°C (cyclohexane).

- (89) 2,4 - Diazido - 6 - (β - methylmercapto-ethylamino)-1,3,5-triazine

- 15 2,4 - Dichloro - 6 - (β - methylmercapto-ethylamino)-1,3,5-triazine can be prepared by the method of J. T. Thurston et al. (J. Amer. Chem. Soc. 73, page 2981 [1963]) from cyanuric chloride and β-methyl-mercapto-ethylamine. It melts at 75° to 77°C (from xylene + cyclohexane).

- 20 35.9 Parts of 2,4 - dichloro - 6 - (β - methylmercapto - ethylamino) - 1,3,5 - triazine were mixed with 60 parts by volume of acetone, 30 parts of sodium azide and 30 parts of water and the whole was stirred for 24 hours at 60°C and then allowed to cool, whereupon 100 parts of water were added. The crystalline product was filtered off, washed with water and crystallized from methanol; it melted at 95° to 96°C.

- (90) In an analogous manner 2,4-diazido-6-sec.butylamino-1,3,5-triazine was prepared from 2,4 - dichloro - 6 - sec.butylamino - 1,3,5-triazine. The product crystallized at a low temperature.

- (91) In an analogous manner 2,4 - dichloro-6 - ethylamino - 1,3,5 - triazine yielded 2,4-diazido - 6 - ethylamino - 1,3,5 - triazine; it is identical with the product No. 78, obtained from 2 - chloro - 4,6 - diazido - 1,3,5 - triazine and ethylamine.

- (92) 2 - Azido - 4,6 - dimethylmercapto - 1,3,5-triazine

- 45 A mixture of 75 parts of methylmercaptan and 107 parts of 2,6-lutidine was added portionwise at 0° to 5°C to a solution of 196 parts of 2,4 - dichloro - 6 - methylmercapto-1,3,5-triazine in 1000 parts by volume of acetone. The mixture was kept for 2 hours at room temperature, then for 14 hours at 50°C, filtered and evaporated. The residue was taken up in 1000 parts by volume of toluene, washed with 2×150 parts of ice water, dried over anhydrous sodium sulfate, filtered and evaporated.

ated. The resulting crude 2 - chloro - 4,6 - dimethylmercapto-1,3,5-triazine was crystallized from hexane and melted at 84° to 86°C.

- 21 Parts of 2 - chloro - 4,6 - dimethylmercapto-1,3,5-triazine, 15 parts of sodium azide, 75 parts by volume of acetone and 50 parts of water were stirred for 24 hours at 60°C. The mixture was then mixed with 200 parts of water. The crystalline product was filtered off, washed with water and crystallized from acetone; it melted at 117° to 118°C.

As described above, 196 parts each of 2,4-

dichloro - 6 - methylmercapto - 1,3,5 - triazine were reacted with the following amounts of mercaptans and alcohols:

- 140 parts of isobutylmercaptan  
50 parts of methanol  
100 parts of isobutanol.

The resulting 2-alkylmercapto- and 2-alkoxy - 4 - chloro - 6 - methylmercapto - triazines respectively were reacted with sodium azide as described above to give rise to the following compounds



R =		X <sub>4</sub> = Cl; m.p. °C	X <sub>4</sub> = N <sub>3</sub> ; m.p. °C
(93)	isobutylmercapto	(b.p. 128—130°, 0.4mm Hg)	liquid
(94)	methoxy	76—77° (b.p. 125—128°, 0.5mm Hg)	70—71° methanol
(95)	isobutoxy	28—30° (b.p. 135—137°, 1.5mm Hg)	liquid

- 25 (96) 2,4 - Diazido - 6 - methoxy - 1,3,5 - triazine

A solution of 36 parts of 2,4-dichloro-6-methoxy-1,3,5-triazine in 70ml of dioxane was stirred dropwise at about 0°C into 39 parts of sodium azide in 150 parts of water, and the mixture was then stirred for 30 minutes at about 20°C. The oil which had settled out was taken up in 200 parts by volume of benzene, dried and filtered. The filtrate was evaporated in a water-jet vacuum at room temperature and diluted with 100 parts by volume of methanol. The product, melting at 58° to 59°C, crystallized out at 0°C.

The following compound was manufactured in a similar manner from 2,4-dichloro-6-methylmercapto-1,3,5-triazine:

- 40 (97) 2,4 - Diazido - 6 - methylmercapto - 1,3,5-triazine which can be crystallized from cyclohexane and melts at 51—53°C.

- (98) 2,4 - Diazido - 6 - isobutyl - 1,3,5 - triazine

A mixture of 20 parts of 2,4-dichloro-6-isobutoxy-1,3,5-triazine, 20 parts of sodium azide and 50 parts by volume of acetone was stirred and mixed with 50 parts of water, whereupon the batch spontaneously heated up to 60°C. The mixture was then further stirred for 14 hours at room temperature.

The product was taken up in 100 parts by volume of toluene and washed twice with water. The solution was evaporated under vacuum at a maximum temperature of 50°C. The residue was pure, liquid 2,4-diazido-6-isobutoxy-1,3,5-triazine.

In a similar manner the following diazides, which are liquid at room temperature, were manufactured from the corresponding 2-alkoxy- and 2-alkylmercapto - 4,6 - dichloro-1,3,5-triazines:



R =	
(99) n-propoxy	(105) n-propylmercapto
(100) isopropoxy	(106) isopropylmercapto
(101) allyloxy	(107) n-butylmercapto
(102) propargyloxy	(108) isobutylmercapto
(103) γ-chloropropoxy	(109) allylmercapto
(104) n-butoxy	

#### EXAMPLE 2

In each experiment, 10 parts of one of the compounds of Example 1 were mixed with 20 parts of dimethylformamide and 10 parts of a condensation product from an anionic surface-active compound (preferably the calcium or magnesium salt of monolauryl benzene monosulfonic acid) with a nonionic surface-active compound (preferably a polyethylene-glycol ether of the monolauryl ester of sorbic acid) and then diluted with xylene to 100cc. The resulting clear solution was suitable for use as a spray broth concentrate and could be emulsified by being poured into water.

#### EXAMPLE 3

(A) In a greenhouse, earthenware pots were filled with earth and the following plants were seeded in them: *Avena sativa*, *Setaria italica*,

*Sinapis arvensis* and *Lepidium sativum*.

The pre-emergence treatment was carried out 1 day after seeding with spray broths prepared according to Example 2, which contained as active substance the compound of No. 9 of Example 1. The amount applied corresponded to 10 kg of active substance per hectare. Evaluation of the results was carried out 20 days after the treatment.

The post-emergence treatment of the plants mentioned above was carried out in a similar manner, but only 10 days after seeding, when 2 to 3 leaves had appeared.

The amount applied corresponded to 5 kg of active substance per hectare. Evaluation of the results was carried out 20 days after the treatment. The results are summarized in the following table

TABLE

Plant tested	Pre-emergence treatment	Post-emergence treatment
<i>Avena sativa</i>	10	10
<i>Setaria italica</i>	9	10
<i>Sinapis arvensis</i>	10	9
<i>Lepidium sativum</i>	10	10

where 0 indicates no effect, 10 means plants completely destroyed.

(B) In the greenhouse, earthenware pots were filled with earth and the seeds of the plants listed in the Table below were sown in them.

- 5 The pre-emergence treatment was carried out 1 day after seeding with the spray broths prepared according to Example 2, containing as active substance the compound No. 12 of Example 1. Amount applied: 4 kg per hectare. Evaluation was carried out 20 days after the treatment.

The post-emergence treatment of the plants mentioned was carried out in identical manner, but only 10 days after seeding when 2 to 3 leaves had appeared. The amount applied corresponded to 4 kg of active substances per hectare. Evaluation was carried out 20 days after the treatment. The results are summarized in the following

15

TABLE

Plant tested	Pre-emergence treatment	Post-emergence treatment
Triticum	9	9
Hordeum	10	8
Sorghum sudanense	9	9
Panicum crus galli	10	10
Poa trivialis	10	10
Dactylis glomerata	10	10
Allium cepa	10	10
Beta vulgaris	10	10
Calendula chrysanth	10	10
Linum usitatissimum	10	10
Brassica rapa	10	10
Daucus carota	10	10
Lactuca sativa	10	10
Medicago sativa	10	10
Soja. max.	8	10
Phaseolus vulgaris	7	9

- 20 where 0 indicates no effect, 10 means plants completely destroyed.

Under the test conditions described under (A) and (B), good to very good herbicidal effects were obtained with the compounds Nos. 1,3,4,5,9,11,13 to 17, 24, 41, 42, 81, 83 to 85, 88 and 97 of Example 1.

- 25 When used for the post-emergence treatment, a selective action against dicotyledons was observed, for example, with the compounds Nos. 105 to 108 of Example 1.

## EXAMPLE 4

The compound Nos. 1,3,10 and 97 of Example 1 displayed a good microbicidal effect, for example against phytopathogenic fungi. Thus, in a concentration of 0.2% of active substance a 100% effect against *Septoria apii* on celery was recorded, and the plants treated did not suffer any appreciable damage.

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## WHAT WE CLAIM IS:—

1. A pesticidal preparation, especially a herbicidal or microbicidal preparation, which

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comprises as active substance, a compound of the general formula



- wherein  $R_1$  represents a halogen atom, an azide radical, an aliphatic hydrocarbon radical containing up to 4 carbon atoms, the group  $-ZX$  (wherein  $Z$  stands for oxygen or sulfur and  $X$  for an aliphatic hydrocarbon radical containing up to 4 carbon atoms,  $R_2$  represents an aliphatic hydrocarbon radical containing up to 4 carbon atoms, the group  $-ZX$  (wherein  $Z$  stands for oxygen or sulfur and  $X$  for an aliphatic hydrocarbon radical containing up to 4 carbon atoms, or represents the group



- (wherein  $A_1$  stands for an aliphatic hydrocarbon radical containing up to 4 carbon atoms, an alkoxyalkyl, hydroxyalkyl, cyanoalkyl or alkylthioalkyl group containing not more than 4 carbon atoms,  $A_2$  stands for hydrogen or one of the radicals mentioned for  $A_1$ , together with a suitable carrier.
2. A preparation as claimed in Claim 1, wherein there is also present a solvent, a diluent, a dispersant, an adhesive and/or another pesticide, especially a herbicide or a fungicide.
3. A preparation as claimed in Claim 1 or 2 which comprises as active substance a compound of the general formula



- wherein  $X_1$  represents a lower alkyl radical containing up to 4 carbon atoms, and  $R$  represents an amino group substituted by a lower alkyl or alkenyl radical containing up to 4 carbon atoms.
4. A preparation as claimed in Claim 3, wherein a compound of the general formula given is present, where  $X_1$  represents a methyl group.

5. A preparation as claimed in Claim 1 or 2, which comprises as active substance a compound of the general formula

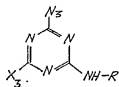


wherein  $X_2$  represents a saturated or unsaturated aliphatic hydrocarbon radical containing up to 4 carbon atoms, an alkoxyalkyl radical containing up to 4 carbon atoms or a chloroalkyl radical containing up to 4 carbon atoms, and  $R$  represents the azide radical or the group



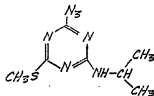
wherein  $A_1$  stands for a saturated or unsaturated aliphatic hydrocarbon radical containing up to 4 carbon atoms, or an alkoxyalkyl radical, and  $A_2$  represents a hydrogen atom or an alkyl radical containing up to 4 carbon atoms.

6. A preparation as claimed in Claim 1 or 2 which comprises as active substance a compound of the general formula



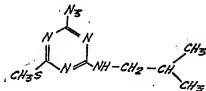
wherein  $R$  represents an alkyl radical containing up to 4 carbon atoms, and  $X_3$  stands for a chlorine atom or the group  $CH_2-S-$  or the azide radical.

7. A preparation as claimed in Claim 6, which comprises as active substance the compound of the formula





8. A preparation as claimed in Claim 6 which comprises as active substance the compound of the formula



- 5 9. A compound of the formula set forth in Claim 1.  
 10. A compound of the formula set forth in Claim 3.  
 11. A compound as set forth in Claim 4.  
 10 12. A compound of the formula set forth in Claim 5.

13. A compound of the formula set forth in Claim 6.

14. A compound of the formula set forth in Claim 7.

15. A compound of the formula set forth in Claim 8.

16. A compound of the formula set forth in Claim 1 and substantially as described in Example 1 herein and in the Tables.

17. A method of selectively combating weeds in a crop area wherein the crop area is treated with a preparation as claimed in Claim 1.

18. A preparation according to Claim 1, and substantially as described in either of Examples 2 or 3 herein.

ABEL & IMRAY,  
 Quality House,  
 Quality Corner, London, W.C.2.

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